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(54) **Monobasic-dibasic acid/salt antifreeze corrosion inhibitor.**

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Description

This invention relates to a metal corrosion inhibitor for use in aqueous solutions, and to antifreeze/coolant compositions containing such a corrosion inhibitor. More particularly, this invention relates to a corrosion inhibitor comprising a combination of monobasic and dibasic acids or the alkali metal, ammonium, or amine salts of said acids, and a hydrocarbyl triazole, and to antifreeze/coolant compositions containing the same.

Automobile engine cooling systems contain a variety of metals, including copper, solder, brass, steel, cast iron, aluminum, magnesium, and their alloys. The possibility of corrosive attack on such metals is high, due to the presence of various ions as well as the high temperatures, pressures, and flow rates found in such cooling systems. The presence of corrosion products within the cooling system can interfere with heat transfer from the engine combustion chambers, which may subsequently cause engine overheating and engine component failure due to excess metal temperatures. See generally Fay, R. H., "Antifreezes and Deicing Fluids," in: Kirk-Othmer Encyclopedia of Chemical Technology (1978 ed.), vol. 3, pp. 79 - 95. It would therefore be generally advantageous if the formation of corrosion products within automobile cooling systems could be controlled or eliminated. It is one object of the instant invention to provide a corrosion inhibitor useful in the prevention and control of corrosion in automobile engine cooling systems containing various metals.

The trend towards improved fuel economy for automobiles has led to the increased use of aluminum and in some cases magnesium for engine and cooling system components. However, it has been found that pitting and crevice corrosion are particularly prevalent in aluminum-containing cooling systems. Many conventional corrosion inhibitor additives used in automobile cooling systems do not provide adequate protection against the pitting and crevice corrosion phenomena found with various aluminum and magnesium alloys. It would therefore be particularly advantageous if the pitting and crevice corrosion phenomena found in automobile cooling systems containing aluminum or magnesium alloys could be controlled or eliminated. It is another object of the instant invention to provide a corrosion inhibitor for use in automobile cooling systems which prevents or controls pitting and crevice corrosion of aluminum and magnesium metal surfaces.

All corrosion inhibitors employed in automobile antifreeze/coolant formulations are gradually depleted by use and the build-up of corrosion products in the cooling system. It would thus be advantageous if the build-up of corrosion products within the system and subsequent corrosion inhibitor depletion or degradation could be controlled or eliminated. It is a further object of the instant invention to provide a corrosion inhibitor which is less prone to depletion or degradation than traditional corrosion inhibitors used in antifreeze/coolant formulations.

It is well known that various monobasic and dibasic acids as well as the salts of such acids are individually effective as corrosion inhibitors when employed in antifreeze/coolant formulations. For example, the use of sodium salts of various monobasic or dibasic acids as mild steel corrosion inhibitors in aqueous solutions is disclosed in Hersch, P., et al., "An Experimental Survey Of Rust Preventives In Water - II. The Screening Of Organic Inhibitors," Journal of Applied Chemistry, vol. 11 (July, 1961), pp. 254-55. The use of a mixture of sodium sebacate (the sodium salt of sebacic acid) and benzotriazole as a useful corrosion inhibitor in engine coolants is disclosed in G. Butler & A.D. Mercer, "Inhibitor Formulations for Engine Coolants," British Corrosion Journal, vol. 12., no. 3 (1977), pp. 171-74.

Several U.S. and foreign patent references disclose the use of various monobasic or dibasic acids, or the salts of such acids, as corrosion inhibitors for use in antifreeze/coolant compositions:

U. S.-A 4,448,702 discloses the use of at least one water-soluble salt of a dicarboxylic acid having at least 3 carbon atoms as a corrosion inhibitor in antifreeze formulations;

U.S.-A 4,382,008 discloses a corrosion inhibitor for use in antifreeze compositions comprising the alkali metal salt of a C₇-C₁₃ dicarboxylic acid, an alkali metal benzoate or toluate, a triazole, an alkali metal borate, and an alkali metal silicate;

U. S.-A 4,342,596 discloses a corrosion inhibiting composition for metals comprising 5-20 parts of a C₈-C₂₀ aliphatic monobasic acid, 0.5-4 parts of a lubricant 0.5-4.0 parts of an amino alkylalkanolamine, 10-35 parts of an aromatic mono- or polycarboxylic acid, and an amine used to form a water-soluble salt with the aromatic acid;

U.S.-A 3,931,029 discloses the use of certain unsaturated cycloalkylene dicarboxylic acids as well as the mono- and di-metal salts, mono- and di-ammonium salts, and mono- and di-amides of such acids as antifreeze additives to inhibit corrosion of contacted solder alloys;

U.S.-A 3,573,225 discloses a corrosion inhibitor containing 50-100 parts of a salt of a C₆-C₁₈ saturated carboxylic acid, 20-200 parts of an alkali metal benzoate, and 1-50 parts of an alkanolamide selected from the reaction products of ethanolamines and a saturated C₆-C₁₈ fatty acid;

GB-A 2,122,598 discloses a metal corrosion inhibitor which comprises at least one C₆ - C₁₀ aliphatic carboxylic acid, at least one C₆ - C₈ polyhydroxycarboxylic acid, and at least one aromatic monocarboxylic acid, in which each of the acids is present as a salt;

Chemical Abstracts, vol. 101, paragraph 115489n (1984) describes Eur. Pat. Appl. EP 112,756, which discloses the use of the alkali metal or amine salts of C₄ - C₁₂ alkyl dicarboxylic acids in combination with C₅-C₁₂ polyols as corrosion inhibitors in antifreeze liquids;

Derwent Abstract of Week C51 for Eur. Pat. 20,042 discloses an aqueous corrosion inhibitor comprising 5-20 parts of an aliphatic C₈-C₂₀ monobasic acid, 10-35 parts of an aromatic mono- or poly- carboxylic acid, 0-4 parts of a lubricant, and an amine forming water soluble salts with the acids; and Chemical Abstracts, vol. 97, paragraph 58367u (1982) describes French Demande FR 2,489,355, which discloses the use of disodium sebacate as a corrosion inhibitor in antifreeze liquids.

The present invention is directed to a novel corrosion inhibitor composition for use in aqueous systems, an antifreeze/coolant concentrate containing the inhibitor composition and aqueous antifreeze/coolant compositions containing the inhibitor composition. It has been found that the components of the corrosion inhibitor composition have a synergistic corrosion inhibiting effect when used in antifreeze/coolant compositions.

The anti-freeze concentrate comprises a water soluble liquid alcohol freezing point depressant and a corrosion inhibitor consisting of carboxylic acids or their salts and a triazole compound, characterised in that the concentrate contains 1) from 0.1 to 15 weight percent, calculated as the free acid, of a C₅ - C₁₆ aliphatic monobasic acid or the alkali metal, ammonium or amine salt thereof, 2) from 0.1 to 15 weight percent, calculated as the free acid, of a C₅ - C₁₆ hydrocarbyl dibasic acid or the alkali metal, ammonium or amine salt thereof, and 3) from 0.1 to 0.5 weight percent of a hydrocarbyl triazole, said weight percentages being based on the amount of the liquid alcohol present.

There is also provided a method of treating aqueous fluids containing a water soluble liquid alcohol freezing point depressant to reduce the corrosion of metals in contact with the fluid by the addition of carboxylic acids or their salts and a triazole compound as corrosion inhibitors, characterised in that 1) from 0.1 to 15 weight percent, calculated as the free acid, of a C₅ - C₁₆ aliphatic monobasic acid or the alkali metal, ammonium or amine salt thereof, 2) from 0.1 to 15 weight percent, calculated as the free acid, of a C₅ - C₁₆ hydrocarbyl dibasic acid or the alkali metal, ammonium or amine salt thereof, and 3) from 0.1 to 0.5 weight percent of a hydrocarbyl triazole are incorporated into the fluid, said weight percentages based on the amount of the liquid alcohol present.

The novel corrosion inhibitor of the instant invention comprises the combination of an aliphatic monobasic acid or the alkali metal, ammonium, or amine salt of said acid, a hydrocarbyl dibasic acid or the alkali metal, ammonium, or amine salt of said acid, and a hydrocarbyl triazole for use as a corrosion inhibitor in aqueous systems, particularly in automobile antifreeze/coolant compositions.

The aliphatic monobasic acid component of the above-described corrosion inhibitor may be any C₅-C₁₆ aliphatic monobasic acid or the alkali metal, ammonium, or amine salt of said acid, preferably at least one C₈-C₁₂ aliphatic monobasic acid or the alkali metal, ammonium, or amine salt of said acid. This would include one or more of the following acids or isomers thereof: octanoic, nonanoic, decanoic, undecanoic and dodecanoic, and mixtures thereof. Octanoic acid is particularly preferred. Any alkali metal, ammonium, or amine can be used to form the monobasic acid salt; however, alkali metals are preferred. Sodium and potassium are the preferred alkali metals for use in forming the monobasic acid salt.

The dibasic acid component of the above-described corrosion inhibitor may be any hydrocarbyl C₅-C₁₆ dibasic acid or the alkali metal, ammonium, or amine salt of said acid, preferably at least one C₈-C₁₂ hydrocarbyl dibasic acid or the alkali metal, ammonium, or amine salt of said acid. Included within this group are both aromatic and aliphatic C₅-C₁₆ dibasic acids and salts, preferably C₈-C₁₂ aliphatic dibasic acids and the alkali metal, ammonium, or amine salts of said acids. This would include one or more of the following acids: suberic, azelaic, sebacic, undecanedioic, dodecanedioic, the diacid of dicyclopentadiene (hereinafter referred to as DCPDDA), terephthalic, and mixtures thereof. Sebacic acid is particularly preferred. Any alkali metal, ammonium, or amine can be used to form the dibasic acid salt; however, alkali metals are preferred. Sodium and potassium are the preferred alkali metals for use in forming the dibasic acid salt.

The hydrocarbyl triazole component of the above-described corrosion inhibitor is preferably an aromatic triazole or an alkyl-substituted aromatic triazole; for example, benzotriazole or tolyltriazole. The most preferred triazole for use is tolyltriazole. The hydrocarbyl triazole is employed at concentrations of about 0.1-0.5 wt.%, preferably about 0.1-0.3 wt.%.

The above-described corrosion inhibitor mixture will most typically be employed in antifreeze formulations as coolants for internal combustion engines. Other applications may include hydraulic fluids, aqueous cutting oils, paints, soluble oils, metal cutting fluids, aircraft deicers, and greases. In these applications, the monobasic and dibasic acid salts may be formed with metal hydroxides including sodium, potassium, lithium, barium, calcium, and magnesium.

The antifreeze formulations most commonly used include mixtures of water and water soluble liquid alcohol freezing point depressants such as glycol and glycol ethers. The glycol ethers which can be employed as major components in the present composition include glycols such as ethylene glycol, diethylene glycol, propylene glycol, and dipropylene glycol, and glycol monoethers such as the methyl, ethyl, propyl and butyl ethers of ethylene glycol, diethylene glycol, propylene glycol, and dipropylene glycol. Ethylene glycol is particularly preferred as the major antifreeze formulation component.

In one preferred embodiment of the instant invention, the above-described corrosion inhibitor is employed in admixture with an aqueous antifreeze/coolant solution comprising 10% to 90% by weight of water, preferably 25% to 50% by weight, a water soluble liquid alcohol freezing point depressant, preferably ethylene glycol, and at least one alkali metal hydroxide which is employed to adjust the pH of the com-

position to a range from about 6.5 to 9.5, preferably from about 7.0 to 9.0.

The approximate proportions of the basic acid components of the above-described corrosion inhibitor solution (based upon the water soluble liquid alcohol freezing point depressant present) are: about 0.1 to 15.0 wt.%, preferably about 0.1 to 2.5 wt.% aliphatic monobasic acid or salt (calculated as the free acid); and about 0.1 to 15.0 wt.%, preferably about 0.1 to 2.5 wt.% hydrocarbyl dibasic acid (calculated as the free acid).

One or more additional conventional corrosion inhibitors may also be employed in combination with the above-described corrosion inhibitor. Such conventional corrosion inhibitors may be employed at concentrations of 0.01-5.0 wt. %, and may be selected from the group comprising: alkali metal borates, alkali metal silicates, alkali metal benzoates, alkali metal nitrates, alkali metal nitrites, alkali metal molybdates, and hydrocarbyl thiazoles. The most preferred conventional corrosion inhibitors for use in combination with the novel corrosion inhibitor of the instant invention are hydrocarbyl triazoles, hydrocarbyl thiazoles, and sodium metasilicate pentahydrate. Organosilane stabilizers may also be employed in conjunction with the sodium metasilicate pentahydrate.

The method of this invention will be further illustrated by the following examples. In the following examples, all percents are weight percents unless otherwise specified.

EXAMPLE 1A

(Control Example)

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 3.9% DCPDDA, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 1B

To the antifreeze formulation of Example 1A, 0.125% neodecanoic acid was added, together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 1C

To the antifreeze formulation of Example 1A, 0.3% neodecanoic acid was added, together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 2A

(Control Example)

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 1.5% sebacic acid, 1.9% terephthalic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 2B

To the antifreeze formulation of Example 2A, 0.1% neodecanoic acid was added, together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 2C

To the antifreeze formulation of Example 2A, 0.3% neodecanoic acid was added, together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 2D

To the antifreeze formulation of Example 2A, 0.5% neodecanoic acid was added, together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 3A

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 1.5% azelaic acid, 1.9% terephthalic acid, and 0.1% neodecanoic acid, as well as sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 3B

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 1.5% azelaic acid, 1.9% terephthalic acid, and 0.3% neodecanoic acid, as well as sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 4A

(Control Example)

An antifreeze formulation was prepared comprising of a major amount of ethylene glycol, 0.2% tolyltriazole, 1.9% terephthalic acid, 1.5% sebacic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 4B

To the antifreeze formulation of Example 4A, 0.1% 2-ethylhexanoic acid was added, together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 4C

To the antifreeze formulation of Example 4A, 0.5% 2-ethylhexanoic acid was added, together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 5

(Comparative Example)

An antifreeze formulation was prepared comprising a major of ethylene glycol, 0.2% tolyltriazole, 3.9% DCPDDA, 0.3% NaNO₃, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 6

(Comparative Example)

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 1.9% terephthalic acid, 1.5% sebacic acid, 0.2% NaNO₃ and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 7

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.1% tolyltriazole, 2.6% neodecanoic acid, 1.5% sebacic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 8

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.1% tolyltriazole, 2.5% 2-ethylhexanoic acid, 1.5% sebacic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 9

(Control Example)

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 5.0% neodecanoic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 10

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 0.9% sebacic acid, 1.15% octanoic acid, 0.6% nonanoic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 11A

(Control Example)

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 2.2% sebacic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 11B

(Control Example)

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 3.3% sebacic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 12

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 0.5% 2-ethylhexanoic acid, 3.9% DCPDDA, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 13A

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 0.3% octanoic acid, 3.9% DCPDDA, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 13B

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 0.5% octanoic acid, 3.9% DCPDDA, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 14

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 3.9% DCPDDA, and 0.3% of a blend of octanoic and decanoic acids, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 15

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 2.14% octanoic acid, 0.86% sebacic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 16

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 2.14% 2-ethylhexanoic acid, 0.86% sebacic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 17

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 1.75% octanoic acid, 1.2% sebacic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 18A

(Control Example)

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 1.0% sebacic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 18B

To the antifreeze formulation of Example 18A, 0.75% octanoic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 18C

To the antifreeze formulation of Example 18A, 1.0% octanoic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 18D

To the antifreeze formulation of Example 18A, 1.15% octanoic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 18E

To the antifreeze formulation of Example 18A, 1.25% octanoic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 18F

To the antifreeze formulation of Example 18A, 1.35% octanoic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 18G

To the antifreeze formulation of Example 18A, 1.50% octanoic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 18H

To the antifreeze formulation of Example 18A, 1.65% octanoic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 18I

To the antifreeze formulation of Example 18A, 1.75% octanoic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 18J

To the antifreeze formulation of Example 18A, 1.85% octanoic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 18K

To the antifreeze formulation of Example 18A, 2.0% octanoic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 19A

(Comparative Example)

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, and minor amounts of sodium tetraborate, sodium benzoate, sodium nitrite, sodium molybdate, sodium metasilicate, organosilane silicate stabilizer, tolyltriazole, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 19B

(Comparative Example)

To the antifreeze formulation of Example 19A, 0.2% sodium nitrate was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 19C

(Comparative Example)

5 To the antifreeze formulation of Example 19A, 0.3% octanoic acid was added.

EXAMPLE 19D

(Comparative Example)

10 To the antifreeze formulation of Example 19A, 0.3% of a mixture of octanoic acid and decanoic acid was added.

EXAMPLE 20A

15 An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 1.0% sebacic acid, 2.0% octanoic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

20 EXAMPLE 20B

To the antifreeze formulation of Example 20A, 0.2% sodium metasilicate pentahydrate and 0.02% organosilane silicate stabilizer was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

25 EXAMPLE 21A

30 An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 0.83% sebacic acid, 1.65% octanoic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 21B

35 To the antifreeze formulation of Example 21A, 0.2% sodium metasilicate pentahydrate and 0.02% organosilane silicate stabilizer was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 22

40 (Control Example)

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 3.5% sebacic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

45 EXAMPLE 23A

(Control Example)

50 An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 1.75% octanoic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 23B

55 To the antifreeze formulation of Example 23A, 0.35% sebacic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 23C

60 To the antifreeze formulation of Example 23A, 0.70% sebacic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

65

EXAMPLE 23D

To the antifreeze formulation of Example 23A, 1.25% sebacic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 23E

To the antifreeze formulation of Example 23A, 1.75% sebacic acid was added together with sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 24

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 1.17% octanoic acid, 1.17% sebacic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 25

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 2.0% octanoic acid, 1.25% sebacic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

EXAMPLE 26

An antifreeze formulation was prepared comprising a major amount of ethylene glycol, 0.2% tolyltriazole, 1.75% nonanoic acid, 1.20% sebacic acid, and sufficient NaOH to modify the pH of the formulation to between 7.0 and 9.0.

Table I sets forth results obtained via the Galvanostatic Pitting Potential Test (Galvanostatic Test) for various examples of the instant invention as well as comparative examples. The Galvanostatic Test gives a measure of the long-term effectiveness of coolants in preventing pitting corrosion attack in aluminum heat exchangers. By applying a current to an aluminum coupon, an accelerated test was developed. In this test, 50 ml of an antifreeze solution (25% solution of the antifreeze formulation in water which contains chloride ions) are added to the test system. A graphite rod is used as the counterelectrode and a standard calomel electrode (SCE) is used for all potential measurements. A current is applied and the most active (most negative) potential (E_G) value observed is taken as the most comparative estimate of pitting potential. The higher (more positive) the E_G value is at a fixed current density, the more effective the antifreeze formulation is in preventing pitting corrosion.

As illustrated by Table I, the combination of monobasic and dibasic acids or the salts of said acids dramatically improves corrosion inhibiting effectiveness as compared with antifreeze/coolant formulations employing only dibasic acids or salts. The addition of as little as 0.1 - 0.5 wt.% of the monobasic acids nonanoic, 2-ethylhexanoic, or octanoic acid to an antifreeze/coolant formulation containing one or more dibasic acids results in great improvement in the pitting protection imparted by the formulation.

Furthermore, the instant invention gives pitting protection superior to that given by the commercially employed corrosion inhibitor NaNO_3 . As illustrated by a comparison of Examples 5 and 13A, 0.3 wt. % octanoic acid provides slightly superior protection from pitting corrosion as compared to 0.3 wt. % NaNO_3 . However, a comparison of Examples 5A and 13 on a molar basis indicates that octanoic acid is more than 1.5 times as effective as NaNO_3 in preventing pitting corrosion.

TABLE I
GALVANOSTATIC PITTING POTENTIAL CORROSION TEST

Example	Monoacid (wt.%)	Diacid (wt.%)	Other Additives (wt.%)	E _g (mv vs. SCE)
1A	—	DCPDPA (3.9%)	Tolytriazole (0.2%); NaOH	-595
1B	Neodecanoic (0.125%)	DCPDPA (3.9%)	Tolytriazole (0.2%); NaOH	-220
1C	Neodecanoic (0.3%)	DCPDPA (3.9%)	Tolytriazole (0.2%); NaOH	-15
2A	—	Terephthalic (1.9%) & Sebacic (1.5%)	Tolytriazole (0.2%); NaOH	-361, -250
2B	Neodecanoic (0.1%)	Terephthalic (1.9%) & Sebacic (1.5%)	Tolytriazole (0.2%); NaOH	-58, +15
2C	Neodecanoic (0.3%)	Terephthalic (1.9%) & Sebacic (1.5%)	Tolytriazole (0.2%); NaOH	+87, +125
2D	Neodecanoic (0.5%)	Terephthalic (1.9%) & Sebacic (1.5%)	Tolytriazole (0.2%); NaOH	+225
3A	Neodecanoic (0.1%)	Terephthalic (1.9%) & Azelaic (1.5%)	Tolytriazole (0.2%); NaOH	-26
3B	Neodecanoic (0.3%)	Terephthalic (1.9%) & Azelaic (1.5%)	Tolytriazole (0.2%); NaOH	+156
4A	—	Terephthalic (1.9%) & Sebacic (1.5%)	Tolytriazole (0.2%); NaOH	-330
4B	2-Ethylhexanoic (0.1%)	Terephthalic (1.9%) & Sebacic (1.5%)	Tolytriazole (0.2%); NaOH	-215
4C	2-Ethylhexanoic (0.5%)	Terephthalic (1.9%) & Sebacic (1.5%)	Tolytriazole (0.2%); NaOH	-5
5	—	DCPDPA (3.9%)	NaNO ₃ (0.3%); Tolytriazole (0.2%); NaOH	-189
6	—	Terephthalic (1.9%) & Sebacic (1.5%)	NaNO ₃ (0.2%); Tolytriazole (0.2%); NaOH	-61
7	Neodecanoic (2.6%)	Sebacic (1.5%)	Tolytriazole (0.1%); NaOH	+8000
8	2-Ethylhexanoic (2.5%)	Sebacic (1.5%)	Tolytriazole (0.1%); NaOH	+1220
9	Neodecanoic (5.0%)	—	Tolytriazole (0.2%); NaOH	+900
10	Nonanoic (0.6%); Octanoic (1.15%)	Sebacic (0.9%)	Tolytriazole (0.2%); NaOH	+2200

TABLE I (continued)
GALVANOSTATIC PITTING POTENTIAL CORROSION TEST

Example	Monoacid (wt.%)	Diacid (wt.%)	Other Additives (wt.%)	E _g (mv vs. SCE)
5				
11A	—	Sebacic (2.2%)	Tolytriazole (0.2%); NaOH	-160
11B	—	Sebacic (3.3%)	Tolytriazole (0.2%); NaOH	+260
10				
12	2-Ethylhexanoic (0.5%)	DCPDDA (3.9%)	Tolytriazole (0.2%);	-143
13A	Octanoic (0.3%)	DCPDDA (3.9%)	Tolytriazole (0.2%); NaOH	-115
15				
13B	Octanoic (0.5%)	DCPDDA (3.9%)	Tolytriazole (0.2%); NaOH	+182
14	Octanoic/Decanoic (0.3%)	DCPDDA (3.9%)	Tolytriazole (0.2%); NaOH	+100
20				
15	Octanoic (2.14%)	Sebacic (0.86%)	Tolytriazole (0.2%); NaOH	+2242
16	2-Ethylhexanoic (2.14%)	Sebacic (0.86%)	Tolytriazole (0.2%); NaOH	+875
25				
17	Octanoic (1.75%)	Sebacic (1.2%)	Tolytriazole (0.2%); NaOH	+2550
18A	—	Sebacic (1.0%)	Tolytriazole (0.2%); NaOH	-101
30				
18B	Octanoic (0.75%)	Sebacic (1.0%)	Tolytriazole (0.2%); NaOH	-375
18C	Octanoic (1.0%)	Sebacic (1.0%)	Tolytriazole (0.2%); NaOH	-632
35				
18D	Octanoic (1.15%)	Sebacic (1.0%)	Tolytriazole (0.2%); NaOH	-105
18E	Octanoic (1.25%)	Sebacic (1.0%)	Tolytriazole (0.2%); NaOH	+595
40				
18F	Octanoic (1.35%)	Sebacic (1.0%)	Tolytriazole (0.2%); NaOH	+150
18G	Octanoic (1.5%)	Sebacic (1.0%)	Tolytriazole (0.2%); NaOH	+1145
45				
18H	Octanoic (1.65%)	Sebacic (1.0%)	Tolytriazole (0.2%); NaOH	+1720
18I	Octanoic (1.75%)	Sebacic (1.0%)	Tolytriazole (0.2%); NaOH	+1337
50				
18J	Octanoic (1.85%)	Sebacic (1.0%)	Tolytriazole (0.2%); NaOH	+1037
18K	Octanoic (2.0%)	Sebacic (1.0%)	Tolytriazole (0.2%); NaOH	+1830
55				
19A	—	—	Sodium tetraborate; Sodium benzoate; Sodium nitrite; Sodium molybdate; Sodium silicate; Silicate stabilizer; Tolytriazole; NaOH	-196
60				

65

TABLE I (continued)
GALVANOSTATIC PITTING POTENTIAL CORROSION TEST

Example	Monoacid (wt.%)	Diacid (wt.%)	Other Additives (wt.%)	E _p (mv vs. SCE)
19B	—	—	0.2% NaNO ₃ + additives of Example 19A	-182
19C	Octanoic (0.3%)	—	Same as Example 19A	+19
19D	Octanoic/Decanoic (0.3%)	—	Same as Example 19A	+116
20A	Octanoic (2.0%)	Sebacic (1.0%)	Tolyltriazole (0.2%); NaOH	+1775
20B	Octanoic (2.0%)	Sebacic (1.0%)	Tolyltriazole (0.2%); Na metasilicate penta- hydrate (0.2%); Organosilane silicate stabilizer (0.02%); NaOH	+1502
21A	Octanoic (1.65%)	Sebacic (0.83%)	Tolyltriazole (0.2%); NaOH	+1342
21B	Octanoic (1.65%)	Sebacic (0.83%)	Tolyltriazole (0.2%); Na metasilicate penta- hydrate (0.2%); Organosilane silicate stabilizer (0.02%); NaOH	+1779

The corrosion inhibiting properties of various examples of the instant invention were also tested via Rapid Cyclic Potentiokinetic Polarization Scanning (RCP). This technique is described in the CEBELCOR (Centre Belge d'Etude de la Corrosion) publication *Rapports Techniques*, vol. 147, R.T. 272 (Aug. 1984). The technique measures rupture or pitting potential (E_R) as well as repassivation potential (E_p). The potentials are measured with a silver reference electrode and a working electrode constructed from the material subject to corrosive attack. The higher (more positive) the E_R value, the more effective a given antifreeze formulation is in preventing pitting corrosion initiation and progress. Similarly, a higher (more positive) E_p value indicates that the particular corrosion inhibitor formulation has a greater ability to repassivate existing pits and crevices. Table II sets forth data obtained from RCP scans with an aluminum working electrode for various examples. As illustrated by the E_R and E_p data obtained, the instant invention encourages a synergistic resistance to pitting and crevice corrosion attack.

Table II compares RCP data obtained for several commercially available antifreeze formulations as well as several examples of the instant invention. Aluminum, copper, solder, steel, and magnesium working electrodes were used to test the corrosion inhibiting properties of the formulations with respect to each of the five metals. Note that E_p and E_R values for the commercial antifreeze formulations are generally much more modest than those obtained for the examples of the instant invention. Note also that Example 22, which is a dibasic (sebacic) acid formulation alone, is not as effective in protecting aluminum and magnesium as the monobasic-dibasic acid/salt combination formulations of Examples 18K, 20B, 23D, 23E, and 24.

The corrosion behavior of several of the formulations of the instant invention as well as comparative examples were tested according to the ASTM D-1384 Glassware Corrosion Test,

TABLE II
 RAPID CYCLIC POTENTIOKINETIC POLARIZATION (RCP)
 SCANS TO DETERMINE CORROSION INHIBITOR EFFECTIVENESS ON ALUMINUM
 (33% w/w antifreeze in hard corrosive water)

Example	Octanoic Acid Concentration (wt. %)	Sebacic Acid Concentration (wt. %)	Rupture Pitting Potential E _R (mv)	Repassivation Potential E _p (mv)
15	2.14%	0.86%	+2150	+550
18K	2.0%	1.0%	+2500	+1500
20B	2.0%	1.0%	+1650	+250
22	—	3.5%	+500	-500
23A	1.75%	—	+900	-750
23B	1.75%	0.35%	+750	+250
23C	1.75%	0.70%	+1750	+550
23D	1.75%	1.25%	+2200	+1500
23E	1.75%	1.75%	>+2500	*
24	1.17%	1.17%	+1250	+500
25	2.0%	1.25%	>+2500	*
26	1.75%	1.20%	>+2500	*
(nonanoic acid)				

* No repassivation or rupture potential data taken.

TABLE III
RCP SCANS TO DETERMINE CORROSION INHIBITOR
EFFECTIVENESS WITH VARIOUS WORKING ELECTRODES
33% w/w antifreeze in hard corrosive water

Antifreeze Formulation	Working Electrode											
	Al		Cu		Solder		Steel		Mg			
	ER (mv)	EP (mv)	ER (mv)	EP (mv)	ER (mv)	EP (mv)	ER (mv)	EP (mv)	ER (mv)	EP (mv)	ER (mv)	EP (mv)
Commercial A	+450	-450	+850	+100	+1100	+1100	+500	+350	+500	+350	-1750	-1800
Commercial B	+350	-350	+600	0	+150	-350	+500	+500	+	+500	+	+
Commercial C	+800	-250	+800	+80	+150	-300	+600	+600	+	+600	+	+
Example 18K	>+2500	+1600	+2500	+2300	+1050	+920	+600	+550	+2000	+500	+2000	-1500
Example 20B	+1650	+2500	+2500	+2000	+1100	+950	+600	+500	+2000	+500	+2000	-1500
Example 22	+500	-500	+2000	+2000	+1300	+1300	+600	+600	-1000	+600	-1000	-1650
Example 23D	+2000	+1500	>+2500	>+2500	+1100	+850	+600	+550	+	+550	+	+
Example 23E	>+2500	+	>+2500	>+2500	+1050	+1000	+600	+600	+	+600	+	+
Example 24	+1250	+500	>+2500	>+2500	+1100	+900	+600	+550	+	+550	+	+

* No data taken.

TABLE IV
ASTM D-1384 GLASSWARE CORROSION TEST
wt. loss (mg/coupon)

EXAMPLE	Cu	Solder	Brass	Steel	Fe	Al
7	2	5	3	0	-1	5
8	2	-3	2	0	-1	4
9	4	10	5	0	-1	20
10	1	0	0	0	-1	-2
11A	3	2	1	-1	-2	5
11B	4	1	2	0	-1	8
15	-1	5	-1	-3	-3	0
16	1	0	1	-1	-3	0
17	1	9	0	0	-1	3
18K	-1	5	-1	-3	-3	0
20B	2	0	2	-1	-1	-2
22	3	2	1	-1	-2	5
25	0.3	2	1	-1.5	-2	-0.2
ASTM spec., Max.	10	30	10	10	10	30

incorporated herein by reference. Table IV sets forth the results obtained. The smaller the weight loss of the metal coupon, the greater the corrosion inhibiting properties of a particular formulation. A negative weight loss signifies a weight increase due to the formation of a protective coating on the coupon. As illustrated by Table IV, the antifreeze formulations of the instant invention provide good corrosion protection for all of the metals tested. In addition, Tables I-III illustrate that the instant invention provides pitting corrosion protection superior to either monobasic or dibasic acid/salt corrosion inhibitors acting alone, or commercial antifreeze/coolant formulations.

It will be evident that the terms and expressions employed herein are used as terms of description and not of limitation. There is no intention, in the use of these descriptive terms and expressions, of excluding equivalents of the features described and it is recognized that various modifications are possible within the scope of the invention claimed.

Claims

1. An anti-freeze concentrate comprising a water soluble liquid alcohol freezing point depressant and a corrosion inhibitor consisting of carboxylic acids or their salts and a triazole compound, characterised in that the concentrate contains 1) from 0.1 to 15 weight percent, calculated as the free acid, of a C₅ - C₁₆ aliphatic monobasic acid or the alkali metal, ammonium or amine salt thereof, 2) from 0.1 to 15 weight percent, calculated as the free acid, of a C₅ - C₁₆ hydrocarbyl dibasic or the alkali metal, ammonium or amine salt thereof, and 3) from 0.1 to 0.5 weight percent of a hydrocarbyl triazole, said weight percentages being based on the amount of the liquid alcohol present.

2. The anti-freeze concentrate according to Claim 1, characterised in that the concentrate contains from 0.1 to 2.5 weight percent, calculated as the free acid, of a C₈ - C₁₂ aliphatic monobasic acid and from 0.1 to 2.5 weight percent, calculated as the free acid, of a C₈ - C₁₂ hydrocarbyl dibasic acid or the alkali metal, ammonium or amine salts of said acids.

3. The anti-freeze concentrate according to Claims 1 or 2, characterised in that the aliphatic monobasic acid is octanoic acid and the dibasic acid is sebacic acid.

4. The anti-freeze concentrate according to any of the preceding Claims, characterised in that the concentrate contains from 0.1 to 0.2 weight percent of tolyltriazole or benzotriazole.

5. The anti-freeze concentrate according to any of the preceding Claims, characterised in that the concentrate contains an alkali metal borate, silicate, benzoate, nitrate, nitrite, molybdate and/or hydrocarbazole as an additional corrosion inhibitor.

6. The anti-freeze concentrate according to Claim 5, characterised in that the additional corrosion inhibitor is present from 0.01 to 5 weight percent.

7. The anti-freeze concentrate according to Claims 5 or 6, characterised in that the additional corrosion inhibitor is sodium metasilicate pentahydrate.

8. The anti-freeze concentrate according to any of the preceding Claims, characterised in that the pH of the concentrate is in the range 6.5 to 9.5.

9. The anti-freeze concentrate according to Claim 8 characterised in that the pH is adjusted by the addition of sodium hydroxide.

10. The anti-freeze concentrate according to any of the preceding Claims, characterised in that the liquid alcohol freezing point depressant is ethylene glycol.

11. An aqueous coolant composition having a depressed freezing point comprising water and from 10 to 90 weight percent of an anti-freeze concentrate according to any of the Claims 1 to 10.

12. A method of treating aqueous fluids containing a water soluble liquid alcohol freezing point depressant to reduce the corrosion of metals in contact with the fluid by the addition of carboxylic acids or their salts and a triazole compound as corrosion inhibitors, characterised in that 1) from 0.1 to 15 weight percent, calculated as the free acid, of a C₅ - C₁₆ aliphatic monobasic acid or the alkali metal, ammonium or amine salt thereof, 2) from 0.1 to 15 weight percent, calculated as the free acid, of a C₅ - C₁₆ hydrocarbyl dibasic acid or the alkali metal, ammonium or amine salt thereof, and 3) from 0.1 to 0.5 weight percent of a hydrocarbyl triazole are incorporated into the fluid, said weight percentages based on the amount of the liquid alcohol present.

Patentansprüche

1. Gefrierschutzmittelkonzentrat, welches ein wasserlösliches flüssigalkoholisches Gefrierpunktniedrigungsmittel und einen Korrosionsinhibitor, der aus Carbonsäuren oder deren Salzen und einer Triazol-Verbindung besteht, umfaßt, dadurch gekennzeichnet, daß das Konzentrat 1) von 0,1 bis 15 Gew.-%, berechnet als freie Säure, einer aliphatischen monobasischen C₅-C₁₆-Säure oder von deren Alkalimetall-, Ammonium- oder Aminsatz, 2) von 0,1 bis 15 Gew.-%, berechnet als freie Säure, einer dibasischen C₅-C₁₆-Kohlenwasserstoffsäure oder von deren Alkalimetall-, Ammonium- oder Aminsatz und 3) von 0,1 bis 0,5 Gew.-% eines Kohlenwasserstofftriazols enthält, wobei besagte Gewichtsprozentanteile auf der Menge des vorhandenen Flüssigalkohols beruhen.

2. Gefrierschutzmittelkonzentrat nach Anspruch 1, dadurch gekennzeichnet, daß das Konzentrat von 0,1 bis 2,5 Gew.-%, berechnet als freie Säure, einer aliphatischen monobasischen C₈-C₁₂-Säure und von 0,1 bis 2,5 Gew.-%, berechnet als freie Säure, einer dibasischen C₈-C₁₂-Kohlenwasserstoffsäure oder der Alkalimetall-, Ammonium- oder Aminsätze besagter Säuren enthält.

3. Gefrierschutzmittelkonzentrat nach den Ansprüchen 1 oder 2, dadurch gekennzeichnet, daß die aliphatische monobasische Säure Oktansäure und die dibasische Säure Sebazinsäure ist.

4. Gefrierschutzmittelkonzentrat nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß das Konzentrat von 0,1 bis 0,3 Gew.-% Tolyltriazol oder Benzotriazol enthält.

5. Gefrierschutzmittelkonzentrat nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß das Konzentrat ein Alkalimetallborat, -silikat, -benzoat, -nitrat, -nitrit, -molybdat und/oder ein Hydrocarbazon als einen zusätzlichen Korrosionsinhibitor enthält.

6. Gefrierschutzmittelkonzentrat nach Anspruch 5, dadurch gekennzeichnet, daß der zusätzliche Korrosionsinhibitor in einer Menge von 0,01 bis 5 Gew.-% vorhanden ist.

7. Gefrierschutzmittelkonzentrat nach den Ansprüchen 5 oder 6, dadurch gekennzeichnet, daß der zusätzliche Korrosionsinhibitor Natriummetasilikatpentahydrat ist.

8. Gefrierschutzmittelkonzentrat nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß der pH des Konzentrats im Bereich 6,5 bis 9,5 ist.

9. Gefrierschutzmittelkonzentrat nach Anspruch 8, dadurch gekennzeichnet, daß der pH durch die Zugabe von Natriumhydroxid eingestellt wird.

10. Gefrierschutzmittelkonzentrat nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß das flüssigalkoholische Gefrierpunktniedrigungsmittel Ethylenglykol ist.

11. Wässrige Kühlmittelzusammensetzung mit einem erniedrigten Gefrierpunkt, welche Wasser und von 10 bis 90 Gew.-% eines Gefrierschutzmittelkonzentrats nach einem der Ansprüche 1 bis 10 umfaßt.

12. Verfahren zum Behandeln wässriger Flüssigkeiten, die ein wasserlösliches flüssigalkoholisches Gefrierpunktniedrigungsmittel enthalten, zur Verringerung der Korrosion von Metallen, die in Kontakt mit der Flüssigkeit stehen, durch den Zusatz von Carbonsäuren oder deren Salzen und einer Triazol-Verbindung als Korrosionsinhibitoren, dadurch gekennzeichnet, daß 1) von 0,1 bis 15 Gew.-%, berechnet als freie Säure, einer aliphatischen monobasischen C₅-C₁₆-Säure oder von deren Alkalimetall-, Ammonium- oder Aminsatz, 2) von 0,1 bis 15 Gew.-%, berechnet als freie Säure, einer dibasischen C₅-C₁₆-Kohlenwasserstoffsäure oder von deren Alkalimetall-, Ammonium- oder Aminsatz und 3) von 0,1 bis 0,5 Gew.-% eines Kohlenwasserstofftriazols in die Flüssigkeit eingemischt werden, wobei besagte Gewichtsprozentanteile auf der Menge des vorhandenen Flüssigalkohols beruhen.

Revendications

1. Concentré pour antigel comportant un alcool liquide, soluble dans l'eau, abaissant le point de congélation et un inhibiteur de corrosion constitué d'acides carboxyliques ou de leurs sels et d'un composé triazole, caractérisé en ce que le concentré contient 1) de 0,1 à 15 pour cent en poids, calculé en acide libre, d'un acide monobasique aliphatique C₅-C₁₆ ou de l'un de ses sels d'un métal alcalin, d'ammonium ou d'amine, 2) de 0,1 à 15 pour cent en poids, calculé en acide libre, d'un acide dibasique d'un groupe hydrocarbyle C₅-C₁₆ ou de l'un de ses sels d'un métal alcalin, d'ammonium ou d'amine, et 3) de 0,1 à 0,5 pour cent en poids d'un triazole d'un groupe hydrocarbyle, lesdits pourcentages en poids étant basés sur la quantité d'alcool liquide présent.

2. Concentré pour antigel selon la revendication 1, caractérisé en ce que le concentré contient de 0,1 à 2,5 pour cent en poids, calculé en acide libre, d'un acide monobasique aliphatique C_8-C_{12} et de 0,1 à 2,5 pour cent en poids, calculé en acide libre, d'un acide dibasique d'un groupe hydrocarbyle C_8-C_{12} ou de l'un des sels d'un métal alcalin, d'ammonium ou d'amine desdits acides.

5 3. Concentré pour antigel selon la revendication 1 ou 2, caractérisé en ce que l'acide monobasique aliphatique est l'acide octanoïque et que l'acide dibasique est l'acide sébacique.

4. Concentré pour antigel selon l'une quelconque des revendications précédentes, caractérisé en ce que le concentré contient de 0,1 à 0,3 pour cent en poids de tolyltriazole ou de benzotriazole.

10 5. Concentré pour antigel selon l'une quelconque des revendications précédentes, caractérisé en ce que le concentré contient un borate, un silicate, un benzoate, un nitrate, un nitrite, un molybdate et/ou un hydrocarbazole d'un métal alcalin en tant qu'inhibiteur de corrosion supplémentaire.

6. Concentré pour antigel selon la revendication 5, caractérisé en ce que l'inhibiteur de corrosion supplémentaire est présent dans une proportion de 0,01 à 5 pour cent en poids.

15 7. Concentré pour antigel selon l'une des revendications 5 ou 6, caractérisé en ce que l'inhibiteur de corrosion supplémentaire est le pentahydrate de métasilicate de sodium.

8. Concentré pour antigel selon l'une quelconque des revendications précédentes, caractérisé en ce que le pH du concentré a une valeur entre 6,5 et 9,5.

9. Concentré pour antigel selon la revendication 8, caractérisé en ce que l'on ajuste le pH par addition d'hydroxyde de sodium.

20 10. Concentré pour antigel selon l'une quelconque des revendications précédentes, caractérisé en ce que l'alcool liquide abaissant le point de congélation est de l'éthylèneglycol.

11. Composition aqueuse de refroidissement présentant un point de congélation abaissé comportant de l'eau et de 10 à 90 pour cent en poids d'un concentré pour antigel conforme à l'une quelconque des revendications 1 à 10.

25 12. Procédé de traitement de fluides aqueux contenant un alcool liquide, soluble dans l'eau, abaissant le point de congélation pour réduire la corrosion des métaux en contact avec le fluide par addition d'acides carboxyliques ou de leurs sels et d'un composé triazole comme inhibiteurs de corrosion, caractérisé en ce que l'on incorpore dans le fluide 1) de 0,1 à 15 pour cent en poids, calculé en acide libre, d'un acide monobasique aliphatique C_5-C_{16} ou de l'un de ses sels d'un métal alcalin, d'ammonium ou d'amine, 2) de 0,1 à 15 pour cent en poids, calculé en acide libre, d'un acide dibasique d'un groupe hydrocarbyle C_5-C_{16} ou de l'un de ses sels de métal alcalin, d'ammonium ou d'amine, et 3) de 0,1 à 0,5 pour cent en poids d'un triazole d'un groupe hydrocarbyle, lesdits pourcentages en poids étant basés sur la quantité d'alcool liquide présent.

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